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TRANSFER OF MOLYBDENUM DISULFIDE TO VARIOUS METALS

by Gilbert C. Barton* and Stephen V. Pepper

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SUMMARY

An investigation was conducted to determine the transfer characteristics of molybdenum disulfide to sputter cleaned surfaces of copper, nickel, gold, and 304 stainless steel. Pin on disk experiments were conducted with molybdenum disulfide single crystals mounted on the end of the pin. The experiments were conducted in a vacuum at room temperature. Auger electron spectroscopy was used to monitor the presence of molybdenum disulfide on the metal surface.

Results of the study indicate that with a single pass of a molybdenum disulfide crystal across a metal surface adhesive transfer of the molybdenum disulfide to the metal occurs. With repeated passes the transferred molybdenum disulfide film increases in thickness. Transfer is not uniform and large particles will transfer when the orientation of the molybdenum disulfide crystals relative to the interface is other than basal. This is accompanied frequently by scoring of the metal surface by the crystallite edges. Adhesion of the films to the metals is greatest with copper and nickel, intermediate with 304 stainless steel, and least with gold, which indicates a chemical effect.

INTRODUCTION

Adherence of molybdenum disulfide to various metal substrates requiring solid film lubrication has been accomplished by a variety of techniques. These include burnishing, binding with resins, in situ reactions, and, most currently, sputter deposition. With both burnishing (ref. 1) and sputter deposition (ref. 2) the adhesion of the molybdenum disulfide to the substrate surface is found to be sensitive to metal species.

Since much of the research on the interaction of molybdenum disulfide with metal surfaces has been done with residual oxides present on the metal surface, it has been

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difficult to identify the nature of molybdenum disulfide - metal interactions. The use of sputter deposition is an exception in that argon bombardment is used to remove surface oxides and other contaminants prior to molybdenum disulfide deposition.

The objective of the present investigation was to examine the transfer characteristics of molybdenum disulfide to oxide-free metal surfaces in a vacuum. Single crystals of molybdenum disulfide (natural molybdenite) were slid on copper, nickel, gold, and 304 stainless steel. Transfer of molybdenum disulfide to the metal surfaces was monitored with Auger electron spectroscopy. Sliding studies were conducted with a pin on disk specimen configuration. The molybdenite single crystals were mounted on the end of the pin.

APPARATUS

The experiments are conducted in a vacuum chamber (fig. 1) which has been described before (ref. 3). The vacuum system is pumped by sorption pumps and an ion pump. Pressure in the vacuum system is read with a hot cathode ionization gage. The vacuum system achieved a pressure of 1×10^{-8} newton per square meter (1×10^{-10} torr) after bakeout at 250° C. The specimens are shown in the apparatus schematic in figure 1. The disk specimen is mounted on a drive shaft which is rotated with a variable speed magnetic drive assembly. The rider specimen is mounted in an electrically insulated holder. Transfer experiments are conducted with the rider specimen loaded against the disk surface. As the disk is rotated, the rider scribes a circular wear track on the flat surface of the disk. The loads used in this investigation were 10 and 100 grams, and the temperature was 23° C. (See ref. 3 for a more detailed description of the apparatus.)

EXPERIMENTAL PROCEDURE

Molybdenum disulfide (MoS_2) single crystals were rubbed on copper, nickel, gold, and 304 stainless steel surfaces under ultrahigh vacuum conditions. The transfer of the MoS_2 onto the metal surfaces were determined by Auger electron spectroscopy (AES). A thin flake of MoS_2 single crystal was bonded with a high-temperature epoxy adhesive onto the end of a 1.0-centimeter-diameter stainless steel pin with an end radius of 2.54 centimeters and then cured at 140° C for 4 hours.

The metal surfaces were initially polished to a mirror finish using standard metallographic techniques. Final polishing of the copper, nickel, and 304 stainless steel was carried out with a 0.05-micrometer aluminum oxide (Al_2O_3) slurry. The metal

disks were 6.5 centimeters in diameter and 1.3 centimeters thick. The gold plated disk was gold ion plated onto a polished 0.2-centimeter 304 stainless steel disk.

During the polishing of the copper samples, an oxide was formed on the surface which was removed by either electropolishing with phosphoric acid or acid etching with a dilute 1:3 solution of nitric acid and water. After the 304 stainless steel disk surfaces were polished, they were cleaned in a 1:1 solution of nitric and hydrofluoric acid for a few seconds. Final cleaning was accomplished with the metal disk in the vacuum apparatus using argon sputtering with the surface cleanliness being indicated by AES spectra.

Rubbing of the MoS_2 single crystal on the metal disks was done at a 100-gram load by rotating the metal disk under the MoS_2 bullet at the wear track speed of approximately 1 millimeter per second. The MoS_2 wear track rotated under the Auger cylindrical mirror analyzer for analysis. An analysis of the wear track was made after 1, 10, 25, and 100 rotations.

RESULTS

Representative AES spectra for MoS_2 transferred after different numbers of MoS_2 passes on the four metals are presented in figures 2(a) to (d). Because of the nonuniform transfer of MoS_2 onto the metal surfaces, the MoS_2 was rubbed at several different radii on each of the metal disks, and repeated several times on different disks.

In addition, 800 MoS_2 passes were made on the copper, gold, and 304 stainless steel surfaces. Figures 3(a), (b), and (c) show a portion of the central region of the wear track on copper, 304 stainless steel, and gold, respectively, after 800 passes of MoS_2. In this case, the MoS_2 build up is complete on the copper, less complete on the stainless steel, and even less complete on the gold. These general results are confirmed by AES spectra after 1, 10, 25, and 100 MoS_2 passes. The spectra show a much faster buildup on copper than on the 304 stainless steel or the gold. The MoS_2 on nickel was perhaps only slightly less than that on copper.

After only one MoS_2 pass a nonuniform MoS_2 film appears on the metal substrate. On copper and gold this film first appears as a faint brown color. On nickel and 304 stainless steel the MoS_2 film is difficult to see visually because of poor contrast with the substrate. With repeated passes, however, the MoS_2 film increases in thickness and becomes easier to detect visually. It is easier to detect with normal than with low-angle incident illumination.

On copper or gold the film appears first brown, then brownish red, reddish purple, purple, bluish purple, blue, and finally the characteristic MoS_2 silver blue color. Figure 4 is a photograph of an etched copper surface after 25 passes of MoS_2. The

streaks of MoS_2 indicated by the double arrow in figure 4 appear brownish red. An area of heavier MoS_2 coverage, indicated by the single arrow in figure 4, appears reddish purple.

On nickel and 304 stainless steel the MoS_2 film appears as a low contrast silver blue film. Figure 5 is a photograph of 304 stainless steel where (a) one pass (fig. 5(a)) and 110 passes (fig. 5(b)) of MoS_2 have been made. In figure 5(a) the MoS_2 film appears as a big streak seen at the upper right of the photograph. Fainter MoS_2 streaks can be seen in the rest of the photograph. In figure 5(b) part of the MoS_2 film is indicated by arrows. The circle in figure 5(b) indicates a fairly large particle of strongly adhering MoS_2. On each of the four metals the strongly adhering MoS_2 films resisted removal by vigorous rubbing with a dry cotton swab or an acetone saturated cotton swab. Most of the MoS_2 flakes, however, are loosely attached to the surface.

Transfer of the MoS_2 film on the copper, nickel, gold, and 304 stainless steel metal substrates is dependent on the alinement of the basal planes of the MoS_2 single crystal with the surface of the metal substrate. The more nearly the basal planes of the MoS_2 single crystal can be oriented parallel with the metal substrate surfaces, the more uniform and heavy the MoS_2 transfer film is. Orienting the MoS_2 single crystal so that its basal planes are edge on, or nonparallel, with the metal substrate surfaces causes gouging of the substrate with little MoS_2 transfer. This orientation effect has been observed by others (refs. 4 to 6).

When gouging and mechanical plowing take place, even after one MoS_2 pass, subsequent MoS_2 rubbing follows the abrasion of the first pass for several following passes. Subsequently, the MoS_2 crystal distorts and edge planes of the MoS_2 crystal move into new locations, and additional plowing of the substrate takes place in new areas.

With a badly distorted MoS_2 crystal with edge planes exposed to the substrate, severe gouging and plowing take place. This is shown in figure 6 for copper that has been rubbed (20 passes) with the basal planes of the MoS_2 crystal oriented nearly 45° to the copper surface. Nevertheless, some MoS_2 had still transferred as was evident from AES spectra, even though it was not optically visible. Gouging of 304 stainless steel by MoS_2 is shown in figure 7. The gouging here appears as a series of wavy lines.

With the MoS_2 basal planes parallel to the metal substrate, occasional localized sticking of large particles (0.1 mm) of MoS_2 is evident. This is especially evident on the copper surface even after one MoS_2 pass (see fig. 8) Although flaking of the MoS_2 crystal was common and most flakes could be easily blown away with compressed air, many MoS_2 particles were strongly adhered. Surrounding many of these adhered MoS_2 particles was a dark purple film of MoS_2. Some of these locally adhered MoS_2 particles resisted displacement by subsequent burnishing and even show burnish marks on

the top of their surface (fig. 9). The adhesion of these tightly adhering MoS_2 particles was examined by breaking them loose with a needle. The deep depression in the surface remaining after removal of the particle indicated that they had been mechanically plowed into the surface.

In general, the transfer film characteristics of MoS_2 single crystal are as follows:

(1) The uniformity of transfer is dependent on how parallel the MoS_2 basal planes are with the metal substrates.

(2) Gouging of the metal surfaces takes place when the basal planes of the MoS_2 are at an acute (nonparallel) angle with the metal surfaces.

(3) The MoS_2 transfers to the metal surface as a thin film with some localized particles even after only one pass.

(4) The deposited MoS_2 film, even after one pass, can be seen on the metal surface.

(5) The MoS_2 film thickness increases with the number of passes.

(6) Flaking of the MoS_2 crystal occurs during the sliding process.

(7) The particles of MoS_2 adhering in localized spots are due to mechanical plowing.

(8) The transfer of MoS_2 is greater on copper than on the nickel.

(9) The transfer of MoS_2 to 304 stainless steel is not as great as on the copper or nickel.

(10) Transfer of MoS_2 on gold is considerably less than to the other metal surfaces.

DISCUSSION

It is difficult to say whether the thinly deposited MoS_2 film that occurs on each metal surface even after only one pass adheres to the surface chemically, is mechanically plowed into the surface, or both. The following observations are, however, relevant. Although care was taken to look for satellite peaks in the sulfur peak that might indicate chemical bonding of the sulfur to the metal substrate, none were found. Although a check was made to see if a "chemical" shift occurred in the 150-volt sulfur peak, none was found. However, a system with higher resolution may reveal a chemical shift. The ductility and softness of gold is, of course, greater than for copper and yet there was clearly less adhesion of MoS_2 to gold than to copper. This is interpreted as a chemical effect.

The fact that relatively large particles of MoS_2 were deeply imbedded in the metal surface after a single pass indicates that mechanical plowing takes place. At a load of only 10 grams the AES spectra indicated as much MoS_2 transfer as was observed with a 100-gram load. This is interpreted as a chemical transfer effect.

CONCLUSIONS

Based on the transfer studies of this investigation with molybdenum disulfide (MoS_2) single crystals sliding on the metals copper, nickel, gold, and 304 stainless steel, the following conclusions were drawn:

1. On all metal surfaces a thin film of MoS_2 is observed even after a single pass of the molybdenum disulfide single crystal over the surface.

2. The MoS_2 film increases in thickness with repeated passes across the surface.

3. Large particle transfer occurs on basal planes during sliding and contributes to nonuniform film formation where mechanical plowing occurs with sliding on the nonbasal orientation.

4. Scoring or gouging of the metal surfaces occurs by nonbasal orientation of the MoS_2.

5. Metal surface chemistry affects film formation and adhesion of MoS_2. The greatest degree of uniform transfer was to copper and nickel, intermediate to 304 stainless steel, and the least to gold.

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506-16.

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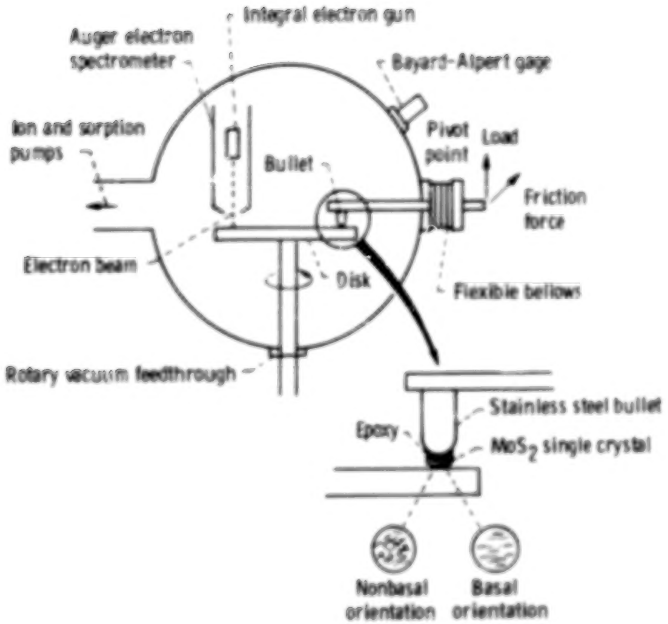
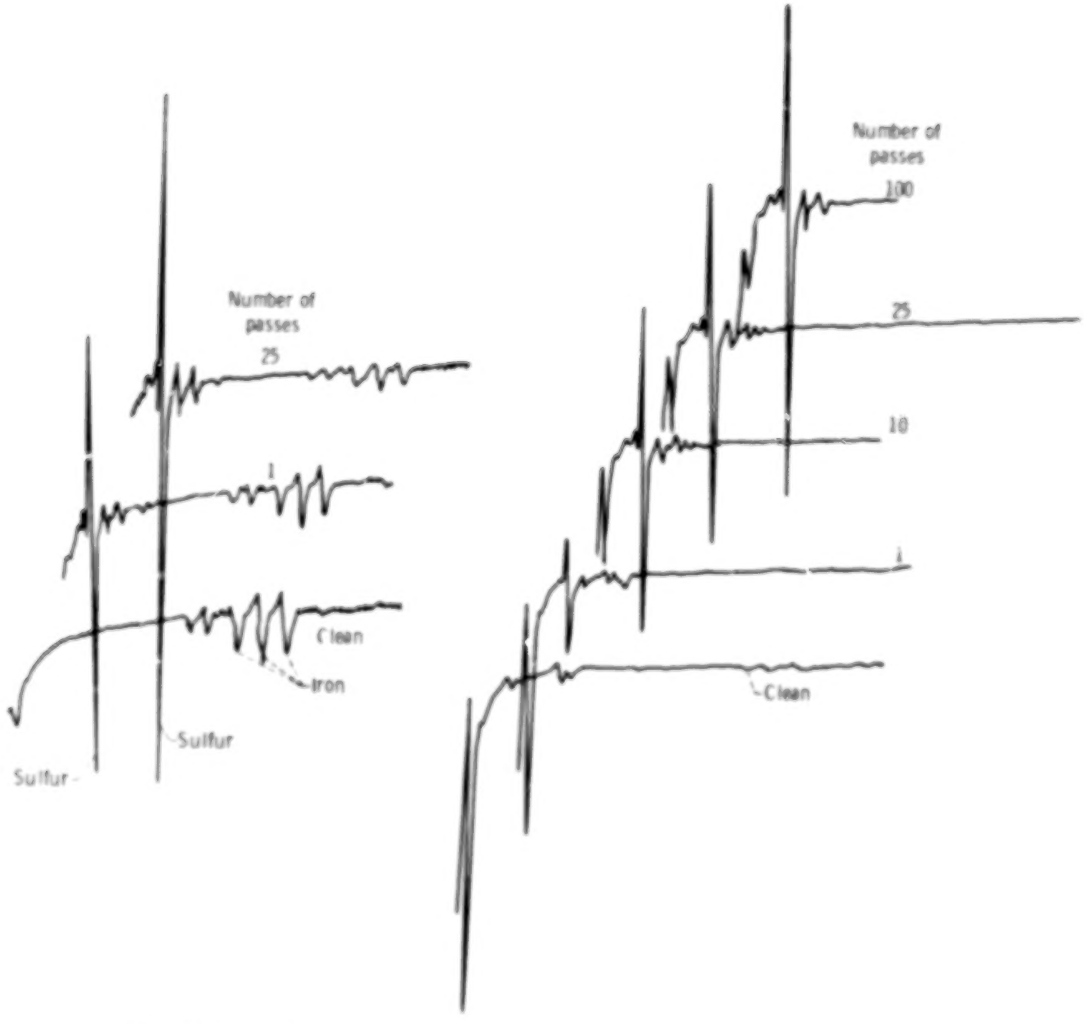


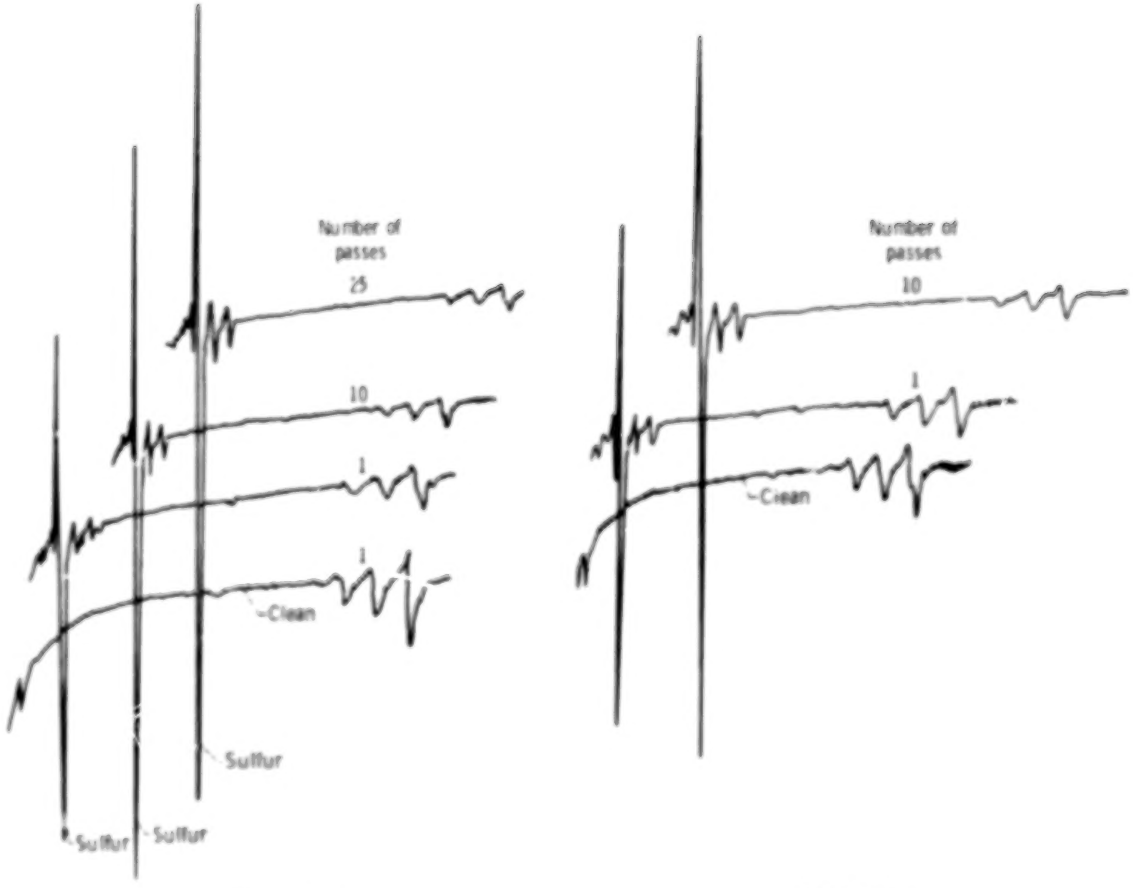
Figure 1. - Friction apparatus with Auger spectrometer.



(c) 304 stainless steel disk.

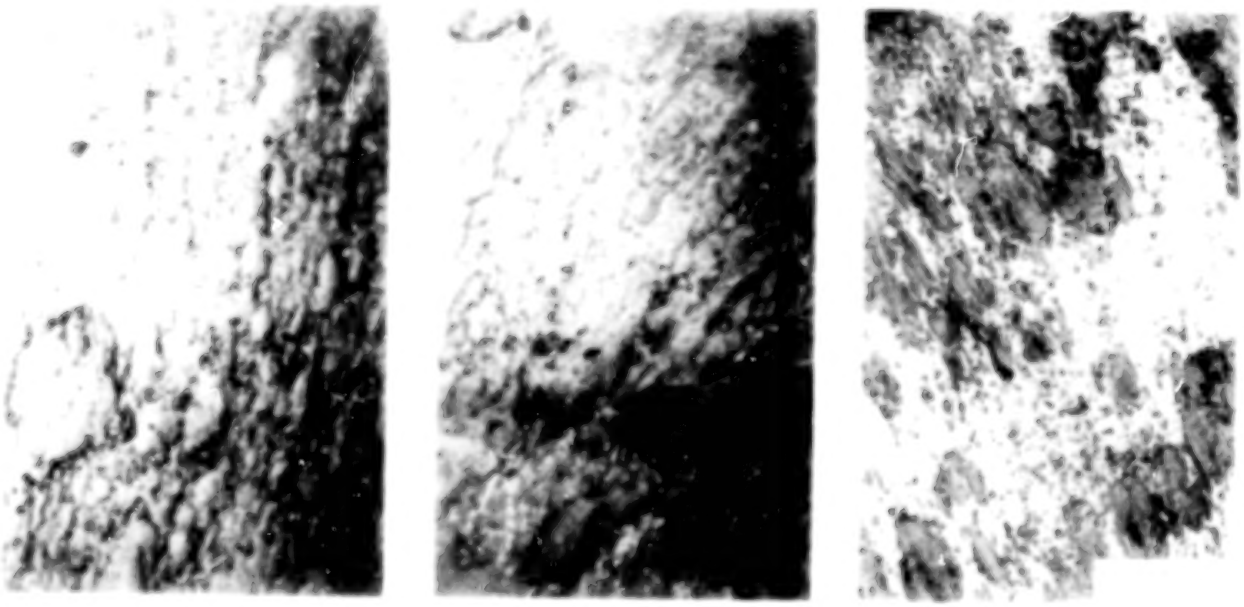
(d) Gold disk.

Figure 2. - Concluded.



(a) Copper disk. (b) Nickel disk.

Figure 2. - Auger electron spectra of metal disks clean and after number of rubbing passes with MoS_2.



(a)

(b) 304 stainless steel

(c) Gold

Figure 3 - Central region of the wear track after 600 MoS_2 passes

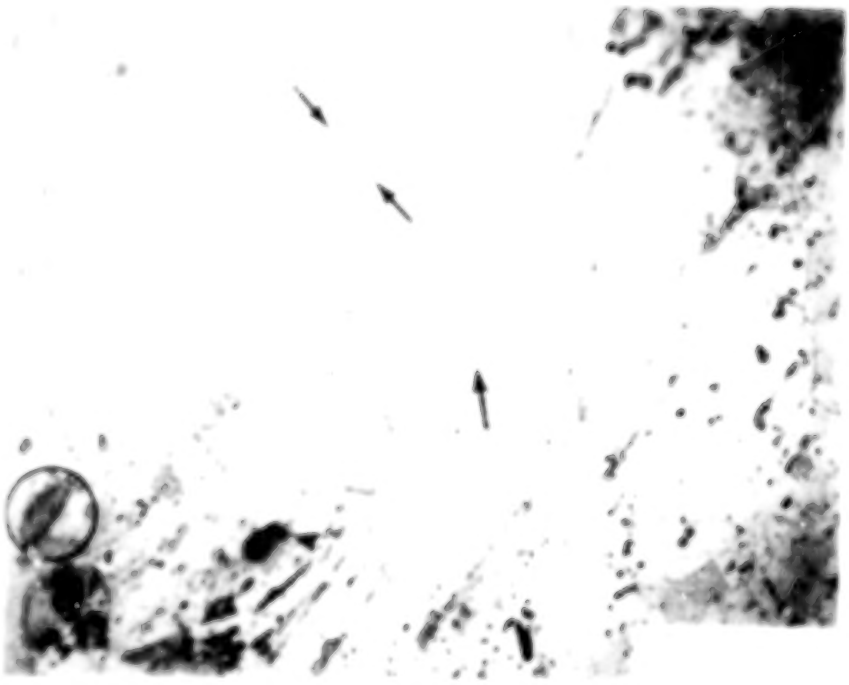
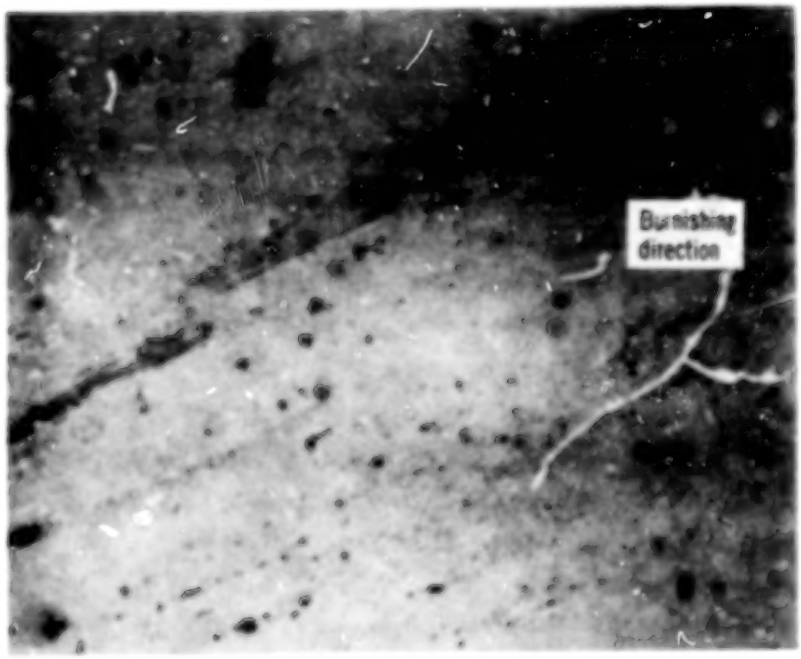
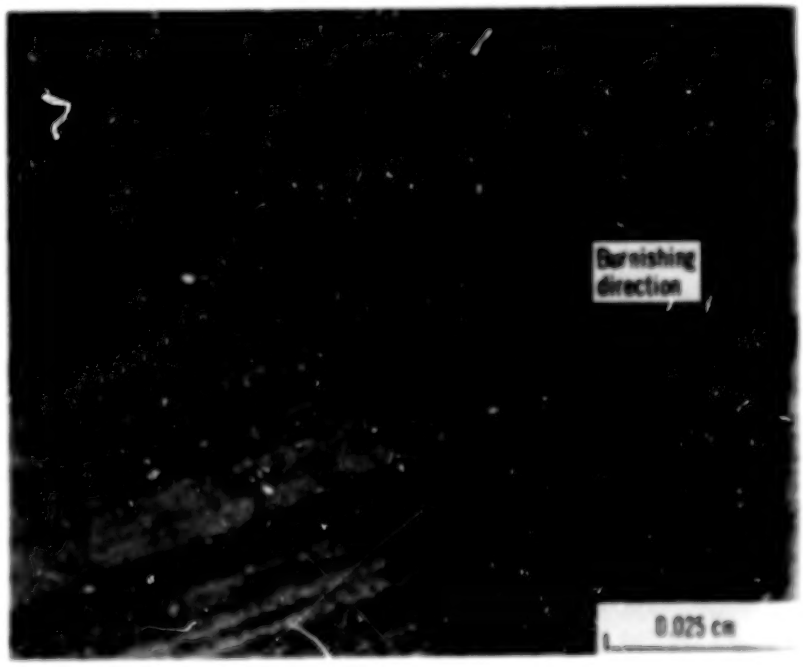


Figure 4 - Etched copper burnished with MoS_2 after 25 passes. On original color photograph brownish-red streaks of MoS_2 are visible (see double arrow). Also shown are more heavily deposited areas of MoS_2 (single arrow). Other thick crusts of MoS_2 (circle) are gouged into irregularities.



(a) Number of passes, 1.



(b) Number of passes, 110.

Figure 5. - MoS_2 onto 304 stainless steel after 1 and 110 passes. MoS_2 streak in (a) is light brown in color. Other MoS_2 streaks in (a) are very faint but still visible. After 110 passes MoS_2 streaks are bluish and more definite, as shown in (b) by arrows. Circle indicates imbedded chunk of MoS_2. Other dark areas are MoS_2.

Figure 6. - Wear track on copper after 20 MoS_2 passes with MoS_2 crystal oriented approximately 45° to copper surface.

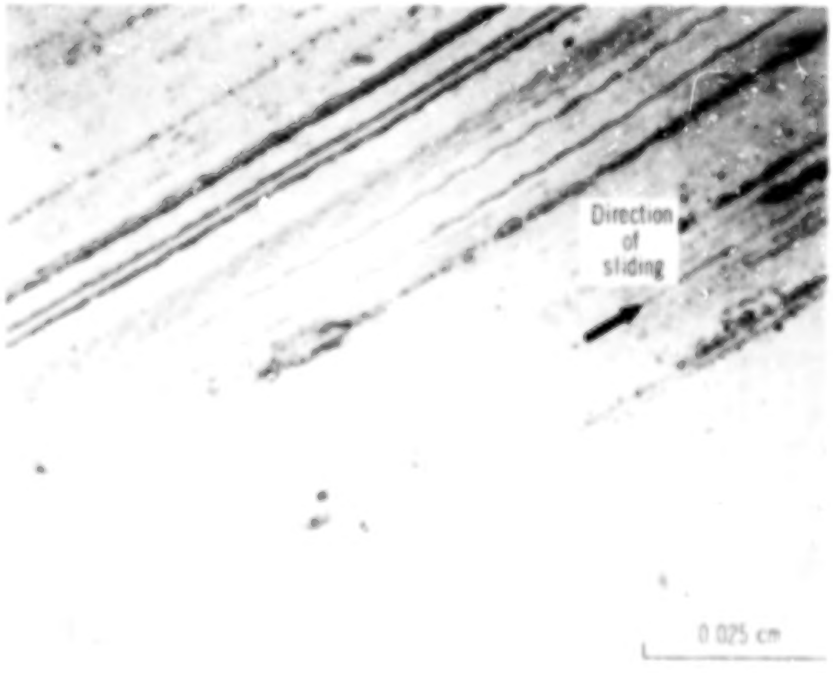


Figure 7. - Wear track on 304 stainless steel by MoS_2 single crystal after 110 passes with gouging appearing as series of wavy lines in photograph.

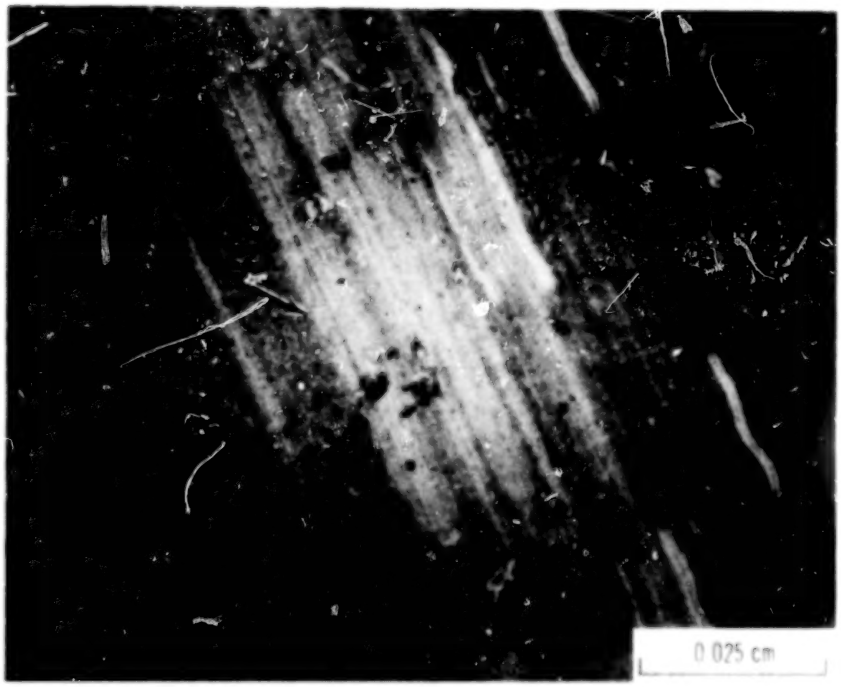
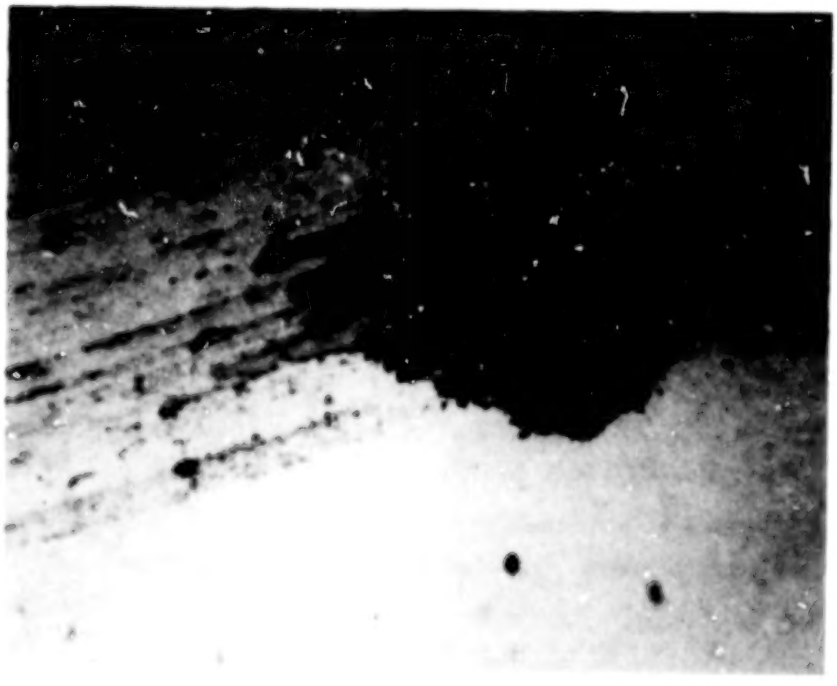


Figure 8. - Chunks of MoS_2 adhering to copper surface after 1 MoS_2 pass. MoS_2 streak shown by arrow appears reddish-purple on original photograph.

(a) Copper after 25 MoS_2 passes.



(b) 304 stainless steel after 100 passes.

Figure 9. - Wear track of MoS_2.

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16. Abstract

Sliding friction experiments were conducted with molybdenum disulfide single crystals in contact with sputter cleaned surfaces of copper, nickel, gold, and 304 stainless steel. Transfer of the molybdenum disulfide to the metals was monitored with Auger electron spectroscopy. Results of the investigation indicate molybdenum disulfide transfers to all clean metal surfaces after a single pass over the metal surface with film thickness observed to increase with repeated passes over the same surfaces. Large particle transfer occurs when the orientation of the crystallites is other than basal. This is frequently accompanied by abrasion of the metal. Adhesion of molybdenum disulfide films occurred readily to copper and nickel, less readily to 304 stainless steel, and even less effectively to the gold, which indicates a chemical effect.

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